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A Scalable Method for Ab Initio Computation of Free Energies in Nanoscale Systems

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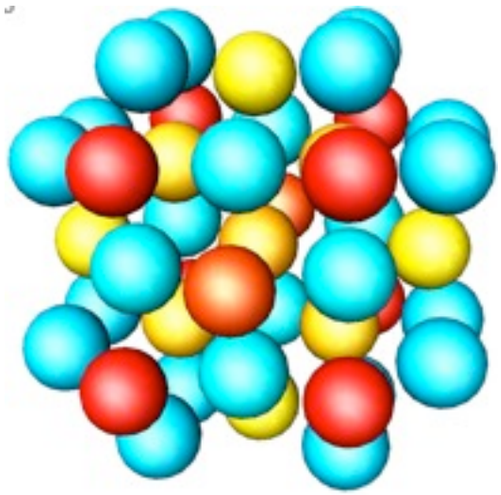
(Spin) Density Functional Theory: The Canonical approach that solves most computational materials/nanoscience

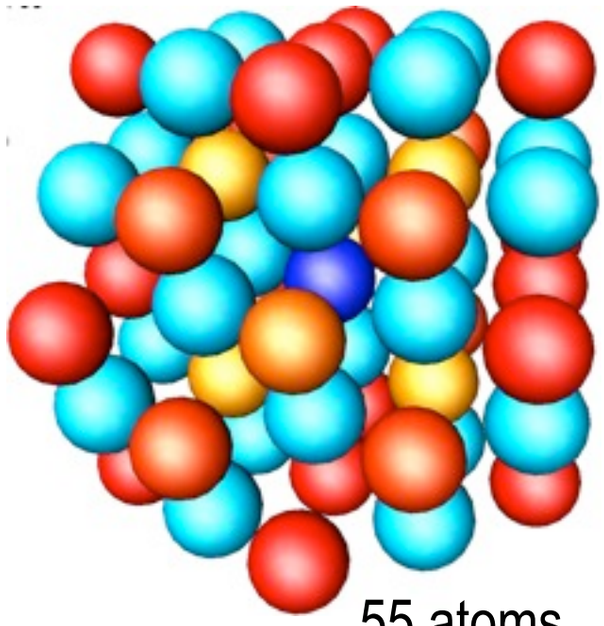
Energy, $E[n_\uparrow, n_\downarrow]$, a unique functional of density $n_\sigma(r) = \sum_i \phi^*_{i,\sigma}(r)\phi_{i,\sigma}(r)$

Kohn-Sham equation: $-\nabla^2\phi_{i,\sigma}(r) + V_\sigma(r)\phi_{i,\sigma}(r) = \epsilon_i\phi_{i,\sigma}(r)$

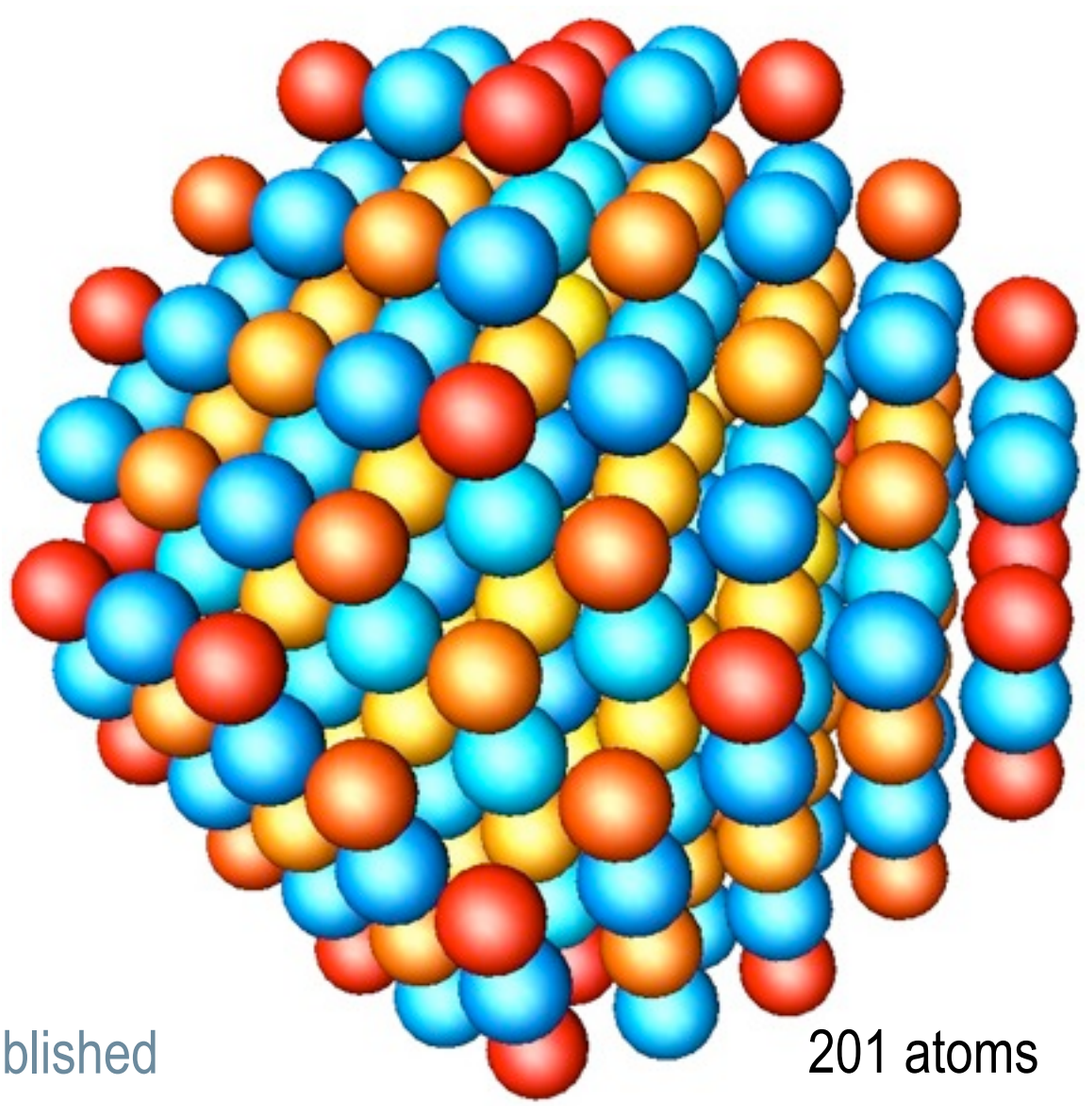
Poisson equation: $\nabla^2 V_e(r) = n_\uparrow(r) + n_\downarrow(r)$



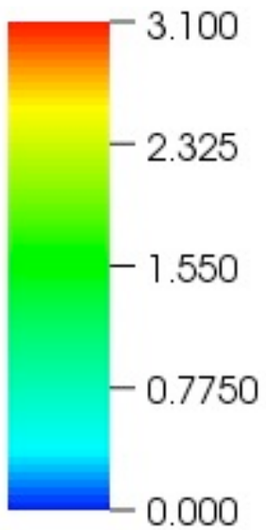
43 atom FePt nanopaticle



55 atoms



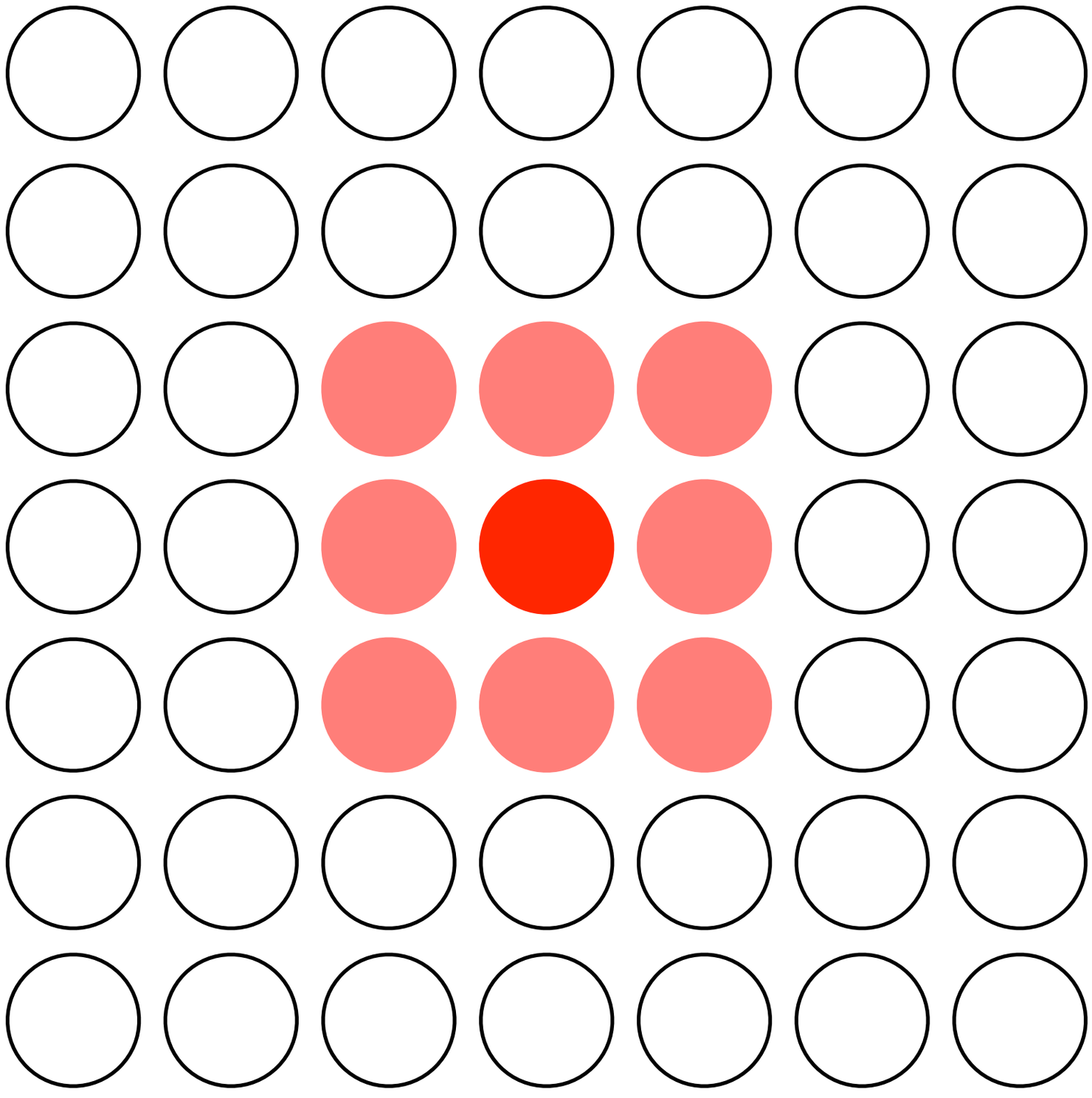
201 atoms



Magnetic moment scale (μ_B)

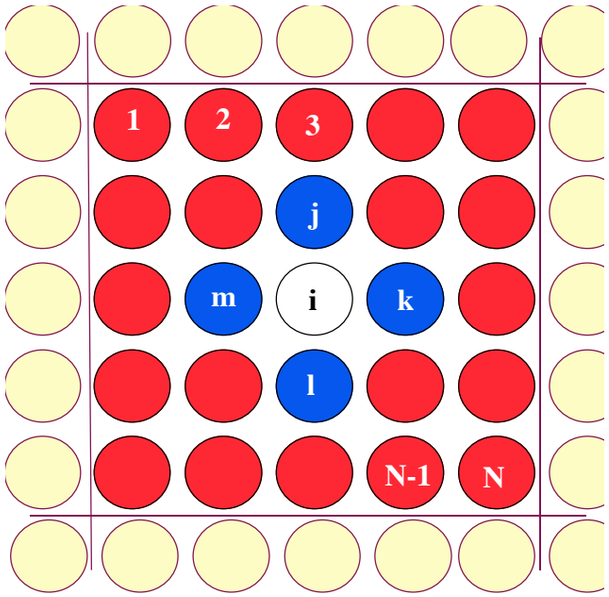
Paul Kent, ORNL, unpublished

Nearsightedness and the locally self-consistent multiple scattering (LSMS) method

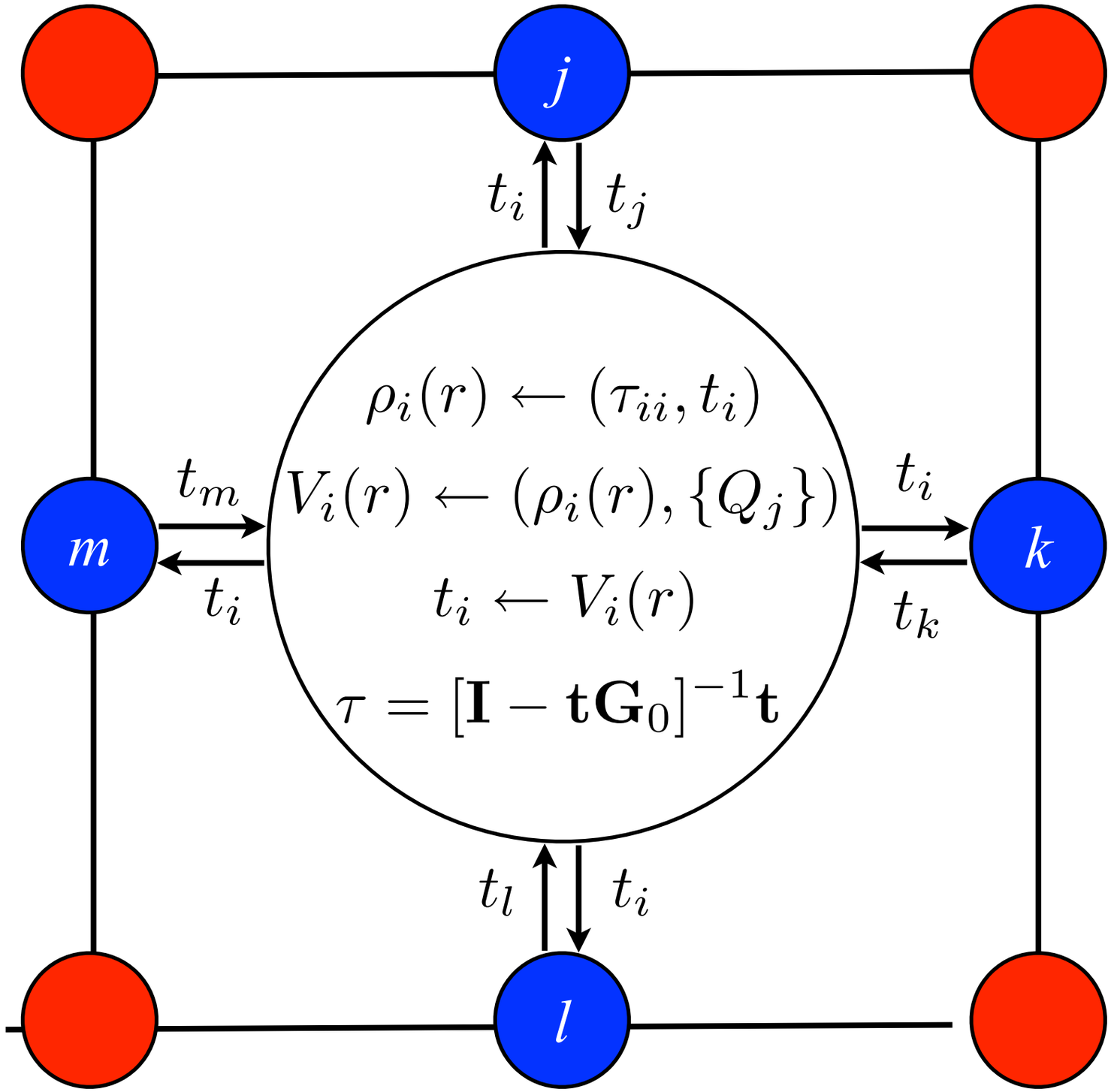


- Nearsightedness of electronic matter - Prodan & Kohn, PNAS **102**, 11635 (2005)
  - *Local electronic properties such as density depend on effective potential only at nearby points.*
- Locally self-consistent multiple scattering method - Wang et al., PRL **75**, 2867 (1995)
  - *Solve Kohn-Sham equation on a cluster of a few atomic shells around atom for which density is computed*
  - *Solve Poisson equation for entire system - long range of bare coulomb interaction*

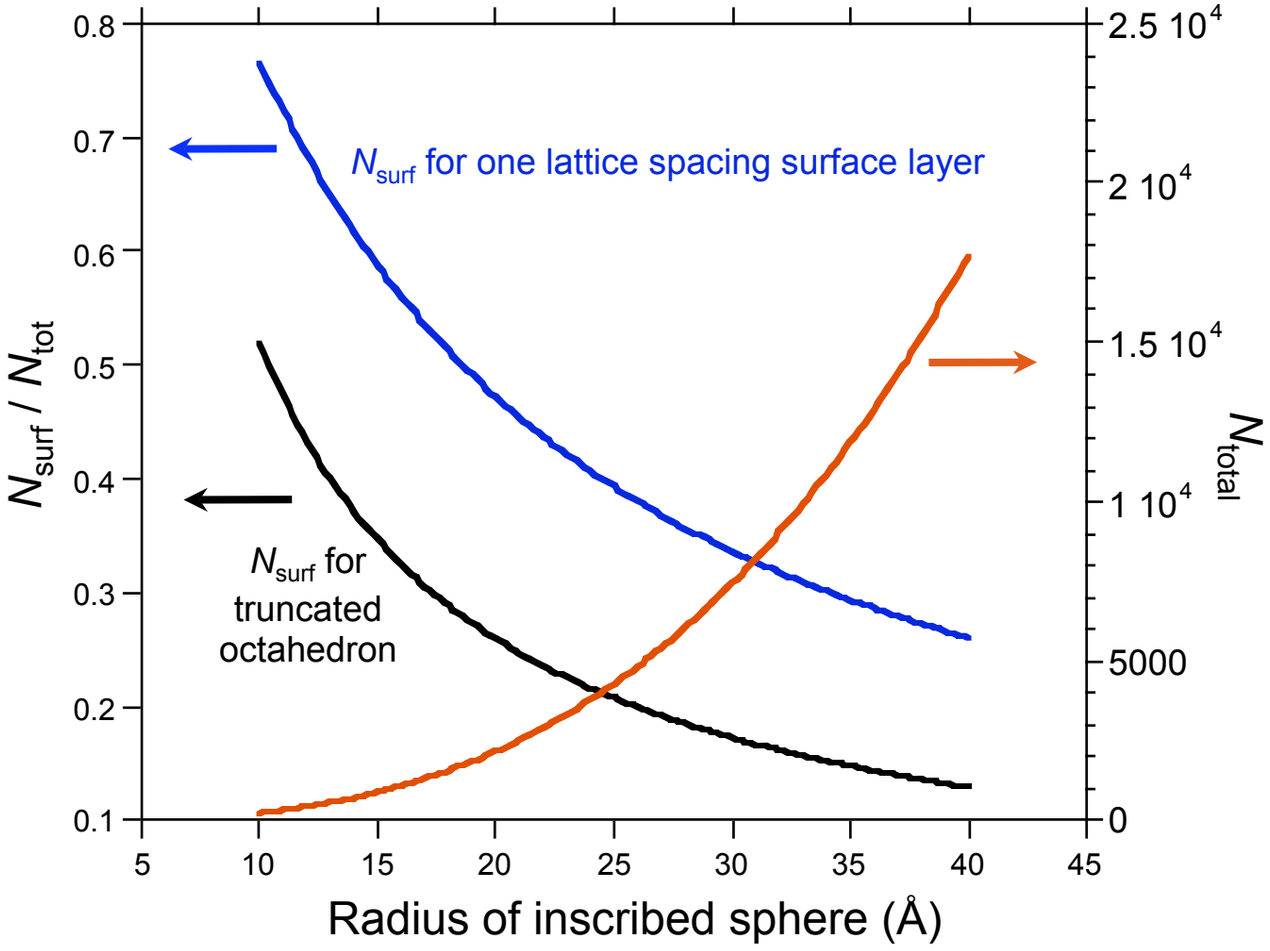
A parallel implementation and scaling of the LSMS method: perfectly scalable at high performance

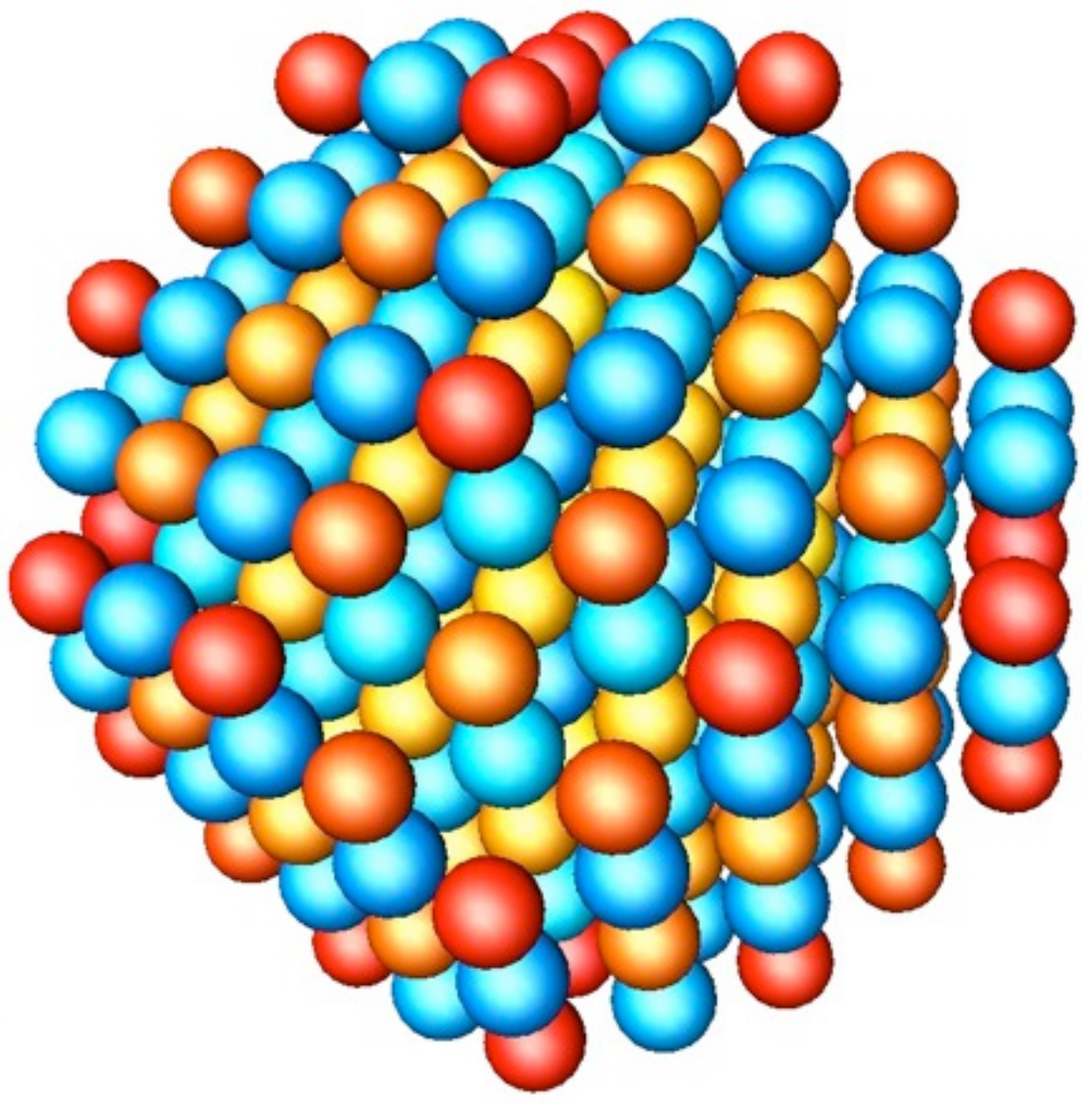


- Need only block i of τ
- $\left(\begin{array}{c|c} A & B \\ \hline C & D \end{array}\right)^{-1} = \left(\begin{array}{c|c} (A - BD^{-1}C)^{-1} & * \\ \hline * & * \end{array}\right)$
- Calculation dominated by ZGEMM
- Sustained performance similar to Linpack

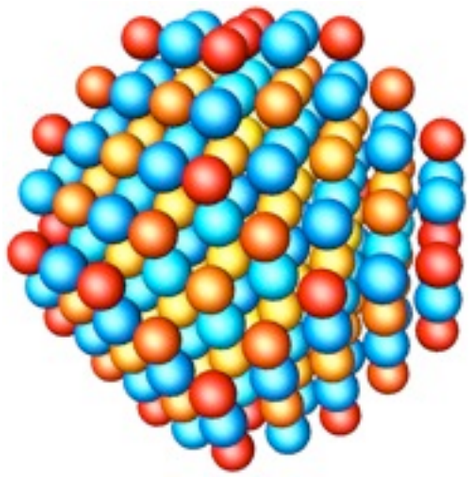


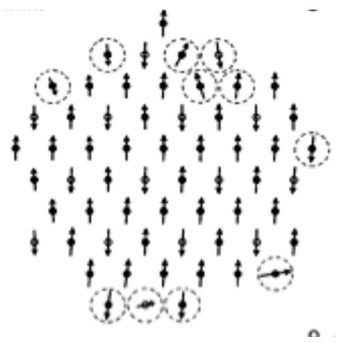
Just looking at larger systems (weak scaling) is not necessarily what is needed





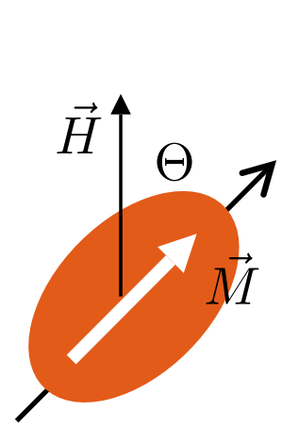
Coarse grained model of a nanoparticle

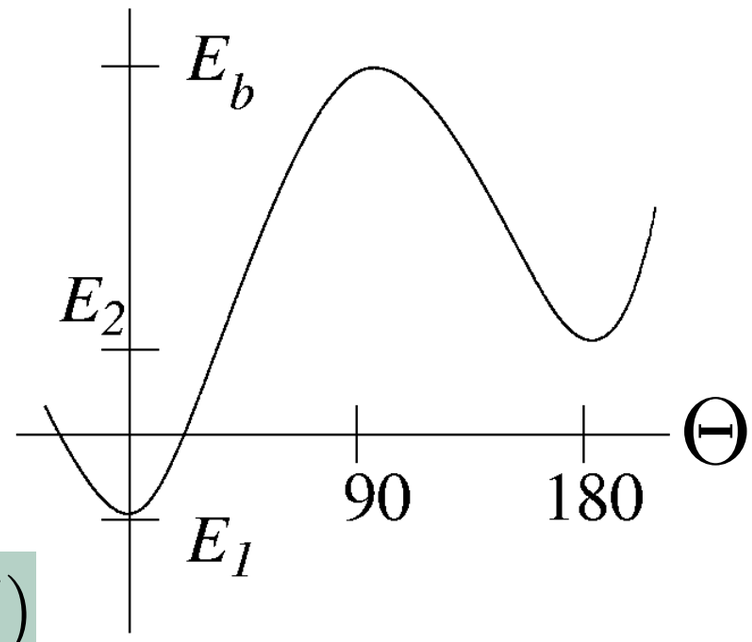


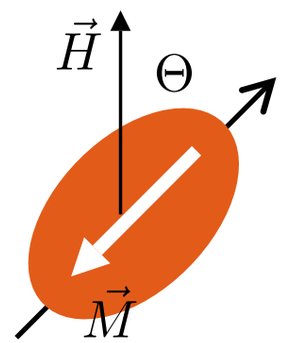


$$\{\vec{m}_1, \vec{m}_2, ..., \vec{m}_N\}$$

$$\vec{M} = 1/N \sum_{i=1}^{N} \vec{m}_i$$







$$F(T, \vec{M}) = E(T, \vec{M}) - k_B T \ln W(E, \vec{M})$$

Realistic model or LDA/GGA based DFT calculation. In most cases $E(T, \vec{M}) \approx E(T = 0, \vec{M})$

With the density of states we would know the free energy at all temperature

Can we compute the density of states?

Metropolis Method

Metropolis et al, JCP **21**, 1087 (1953)

$$Z = \int e^{-E[\mathbf{x}]/k_{\mathrm{B}}T} d\mathbf{x}$$

Compute partition function and other averages with configurations that are weighted with a Boltzmann factor

Sample configuration where Boltz-mann factor is large.

1. Select configuration

$$E_i = E[\mathbf{x}_i]$$

2. Modify configuration (move)

$$E_f = E[\mathbf{x}_f]$$

3. Accept move with probability

$$A_{i\to f} = \min\{1, e^{\beta(E_i - E_f)}\}$$

Wand-Landau Method

Wang and Landau, PRL **86**, 2050 (2001)

$$Z = \int W(E) e^{-E/k_{\mathrm{B}}T} dE$$

If configurations are accepted with probability $1/W$ all energies are visited equally (flat histogram)

1. Begin with prior estimate, eg $W'(E) = 1$

2. Propose move, accepted with probability

$$A_{i\to f} = \min\{1, W'(E_i)/W'(E_f)\}$$

3. If move accepted increase DOS

$$W'(E_f) \to W'(E_f) \times f \qquad f > 1$$

4. Iterate 2 & 3 until histogram is flat

5. Reduce $f \to f = \sqrt{f}$ and go back to 1

Metropolis Method

$$Z = \int e^{-E[\mathbf{x}]/k_{\mathrm{B}}T} d\mathbf{x}$$

Sample configuration space with probability

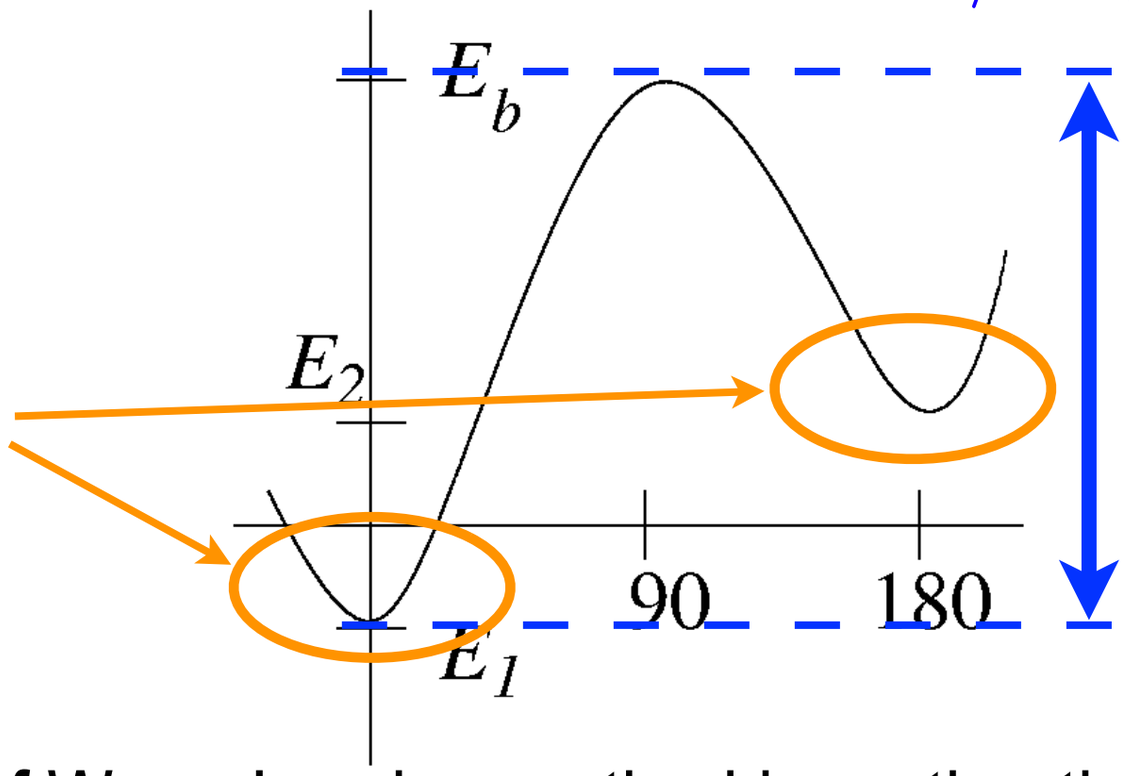
$$e^{-E[\mathbf{x}]/k_{\mathrm{B}}T}$$

Samples mainly regions around energy minima

Wand-Landau Method

$$Z = \int W(E) e^{-E/k_{\mathrm{B}}T} dE$$

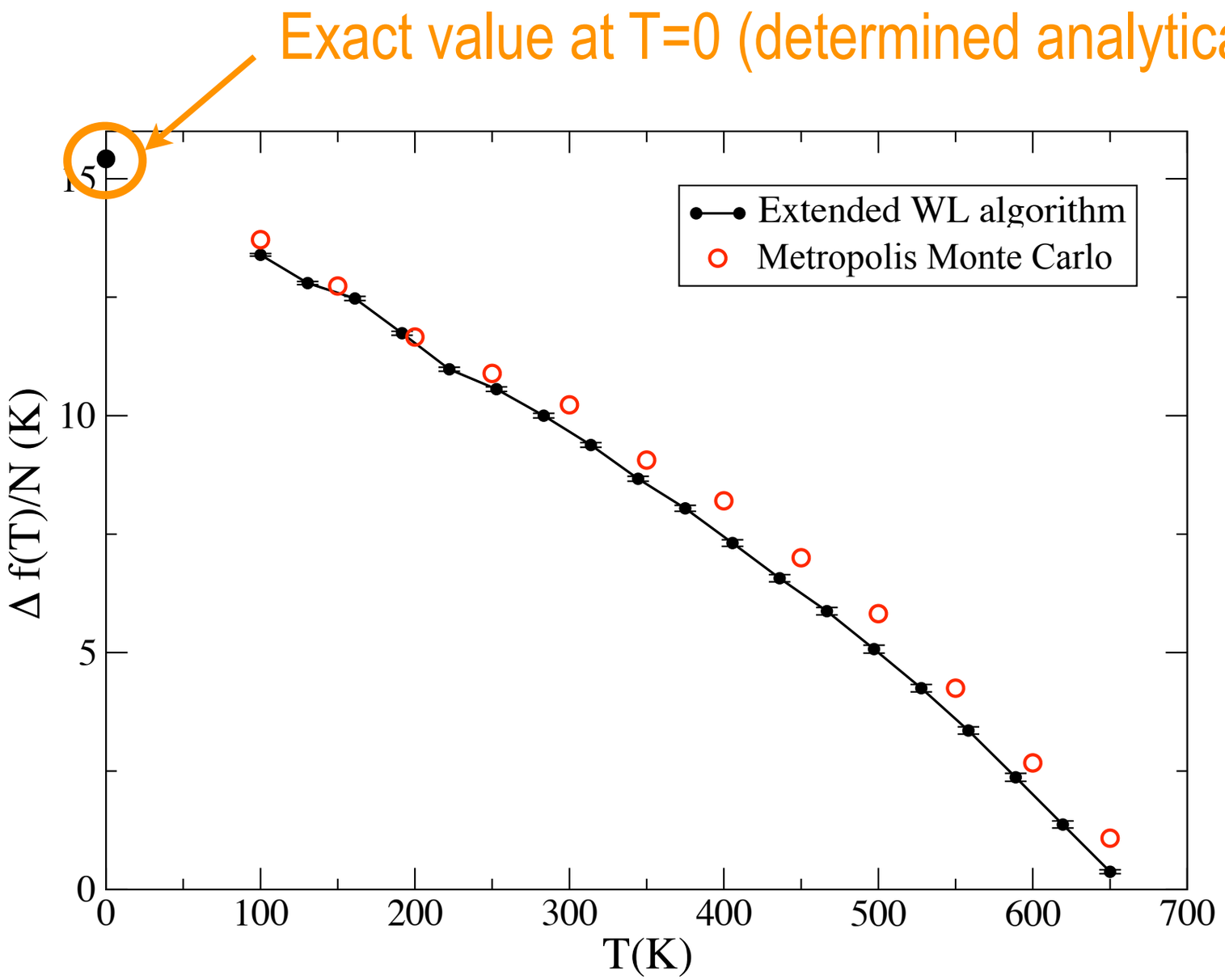
$$1/W(E[\mathbf{x}])$$



Samples all energies equally -

Check validity of Wang-Landau method by estimating barrier hight from Metropolis MC and fitting to $KV \sin^2 \Theta$

Quantitative test for bulk model of FePt

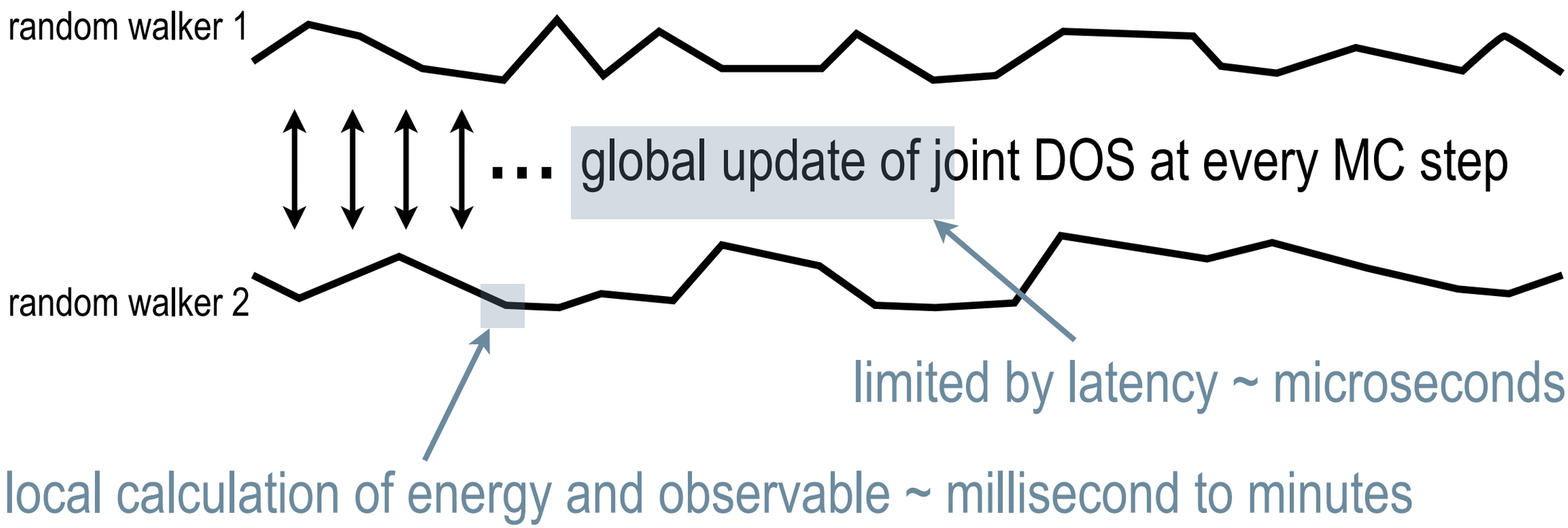


Not quite embarrassingly parallel

Metropolis MC acceptance: $$A_{i\to f} = \min\{1, e^{\beta(E_i - E_f)}\}$$

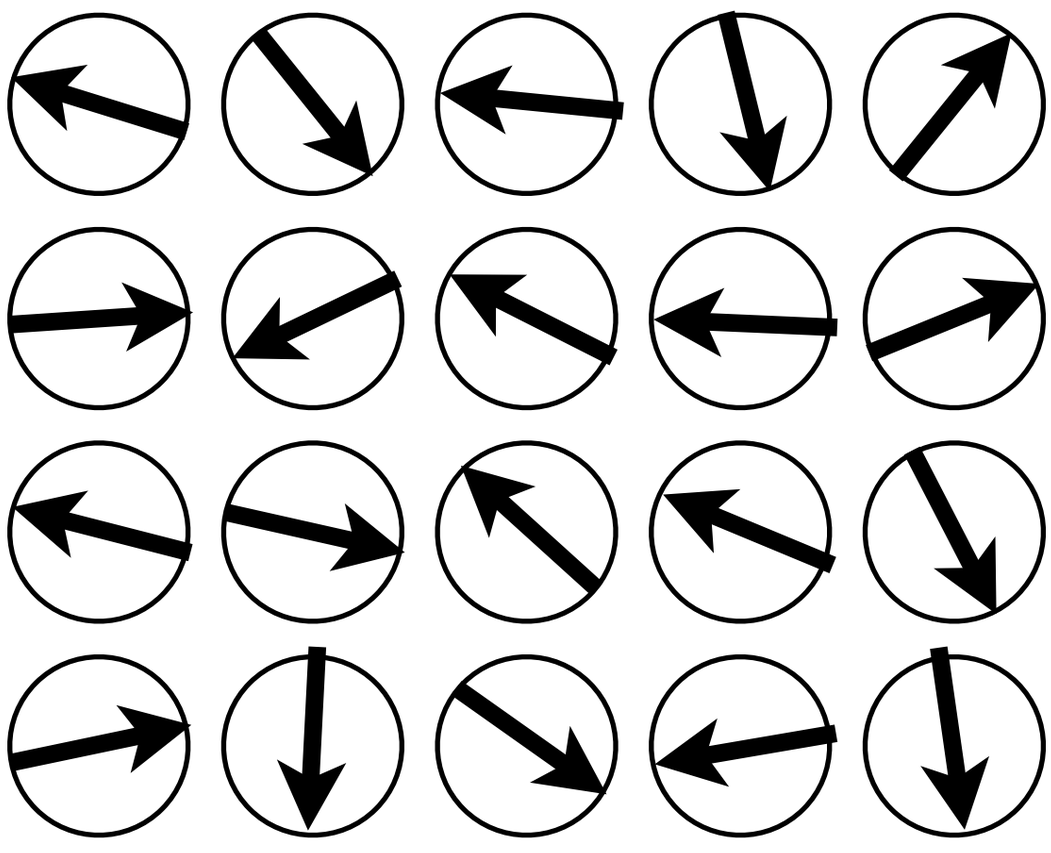
Wang-Landau acceptance:

$$A_{i\to f} = \min\{1, e^{\alpha(w_\alpha(x_f) - w_\alpha(x_i)}\}$$



Test problem: *ab initio* simulation of magnetism in Fe

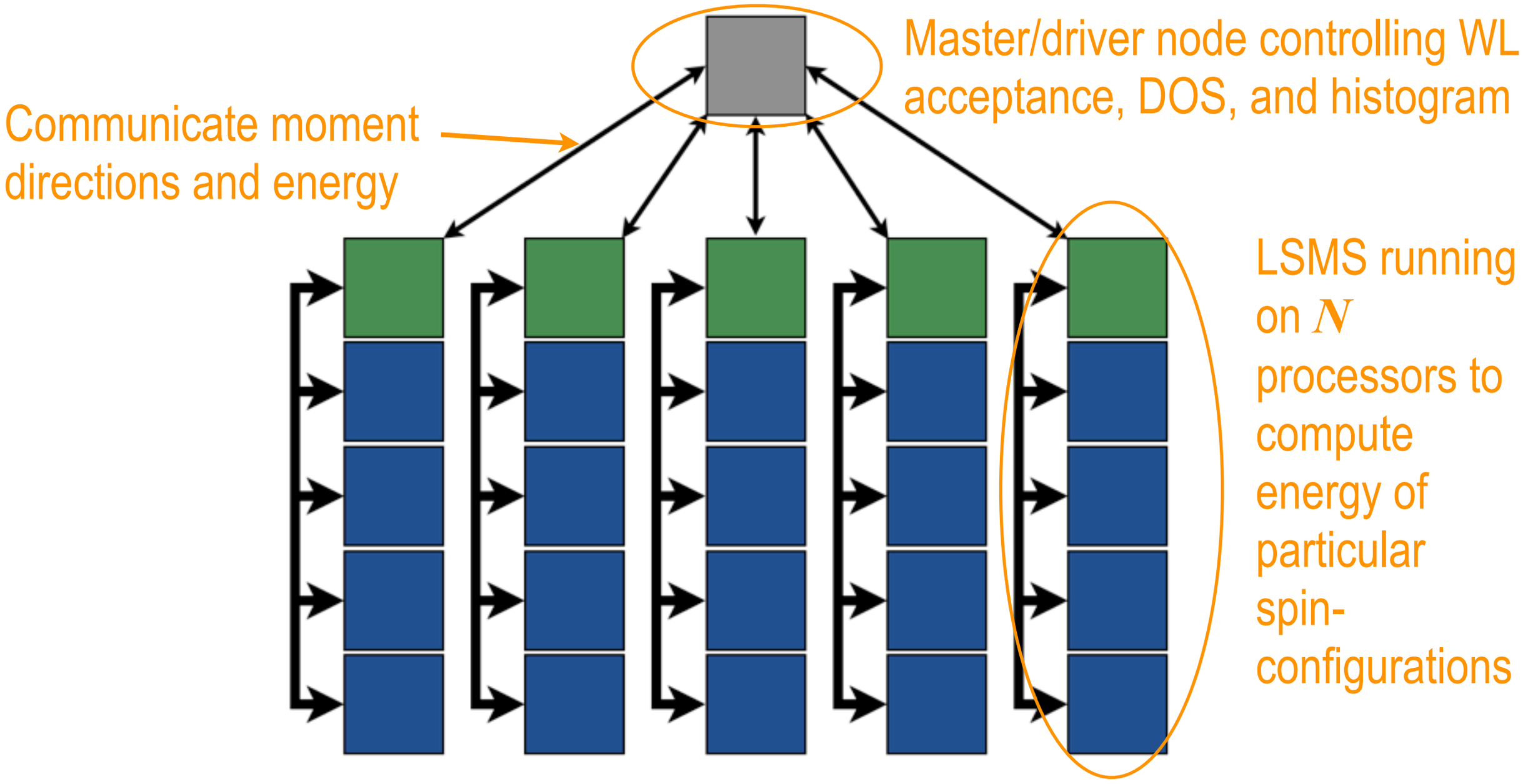
- Robust local magnetic moment
  - Well reproduced by LDA calculation
- Ferromagnetic transition temperature T_c=1050K
  - LDA + mean field on magnetic fluctuations overestimates T_c
  - Adding Onsager cavity field corrections improves results
  - What would a full *ab initio* Monte Carlo simulation give for T_c?



Excellent test for WL-LSMS method:

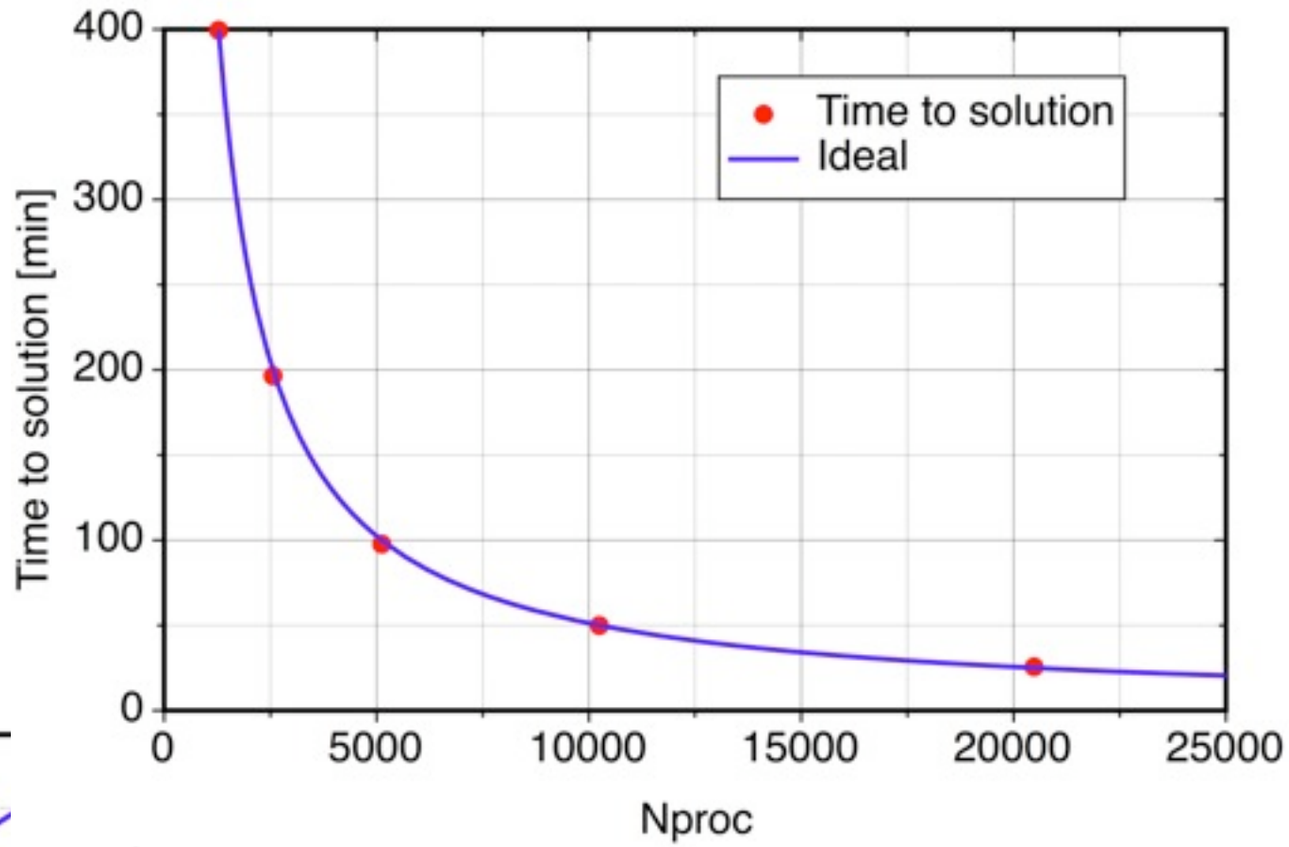
- Bulk Fe with N atoms (hundreds) in unit cell
- Sample non-collinear magnetic moment configurations $\{\vec{m}_1, \vec{m}_2, \ldots, \vec{m}_N\}$
- Compute energy with LSMS method using (LSDA) and frozen potential approx.
- Accumulate density of states with extended Wang Landau algorithm

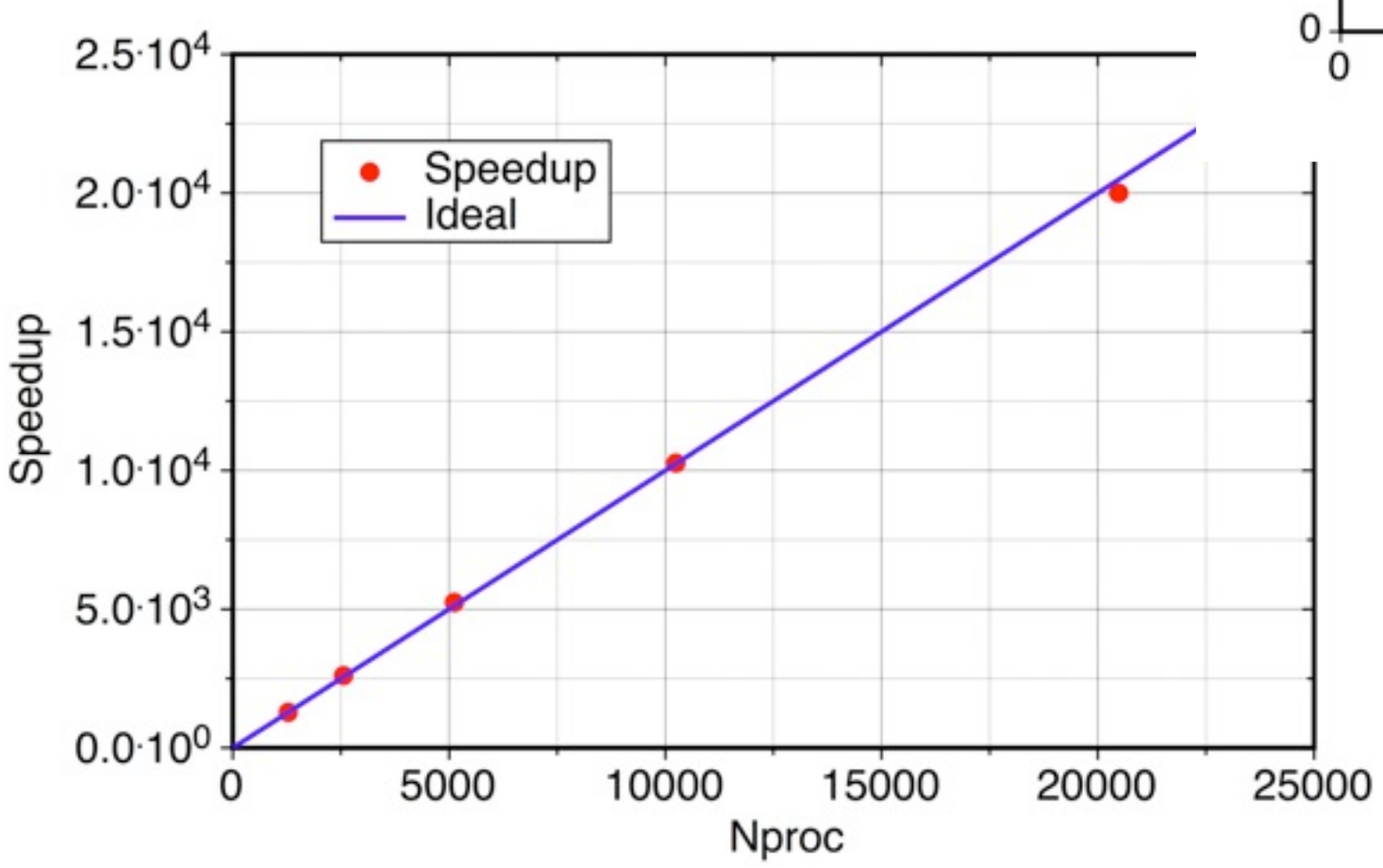
Organization of the WL-LSMS code using a master-slave approach



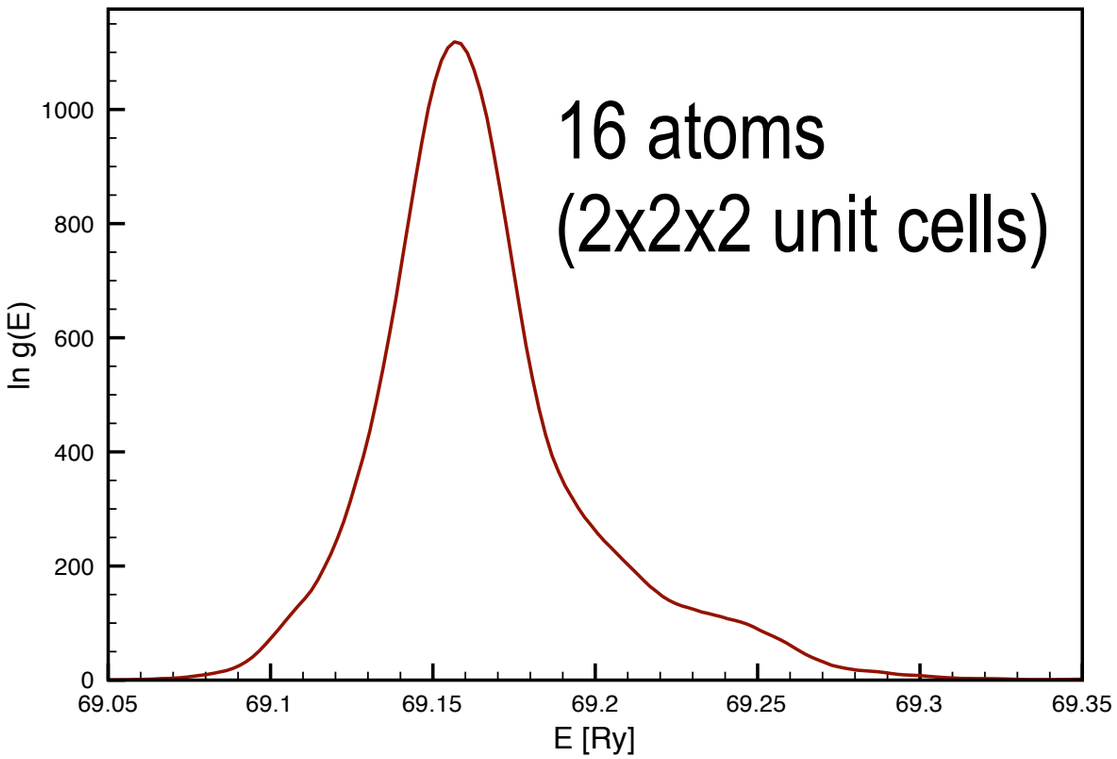
Scaling test with WL-LSMS code

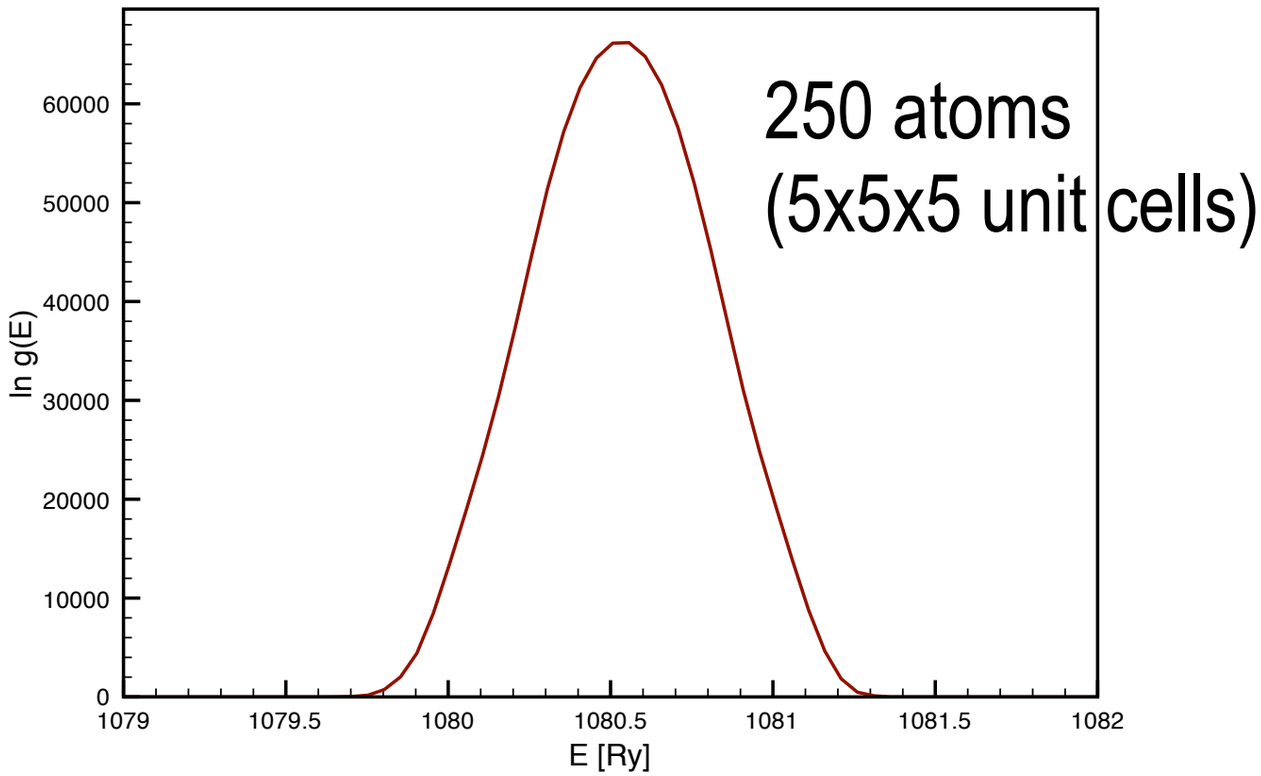
N = 128 Fe atoms and 800 Monte Carlo samples running on Cray XT4 (Jaguar)





What it takes to compute a converged DOS on a Cray XT5





	16 atoms	250 atoms
WL walkers	200	400
total cores	3,208	100,008
WL samples	23,200	590,000
CPU-core hours	12,300	4,885,720

Just 2 days!!!

With the DOS we have the partition function and everything else!

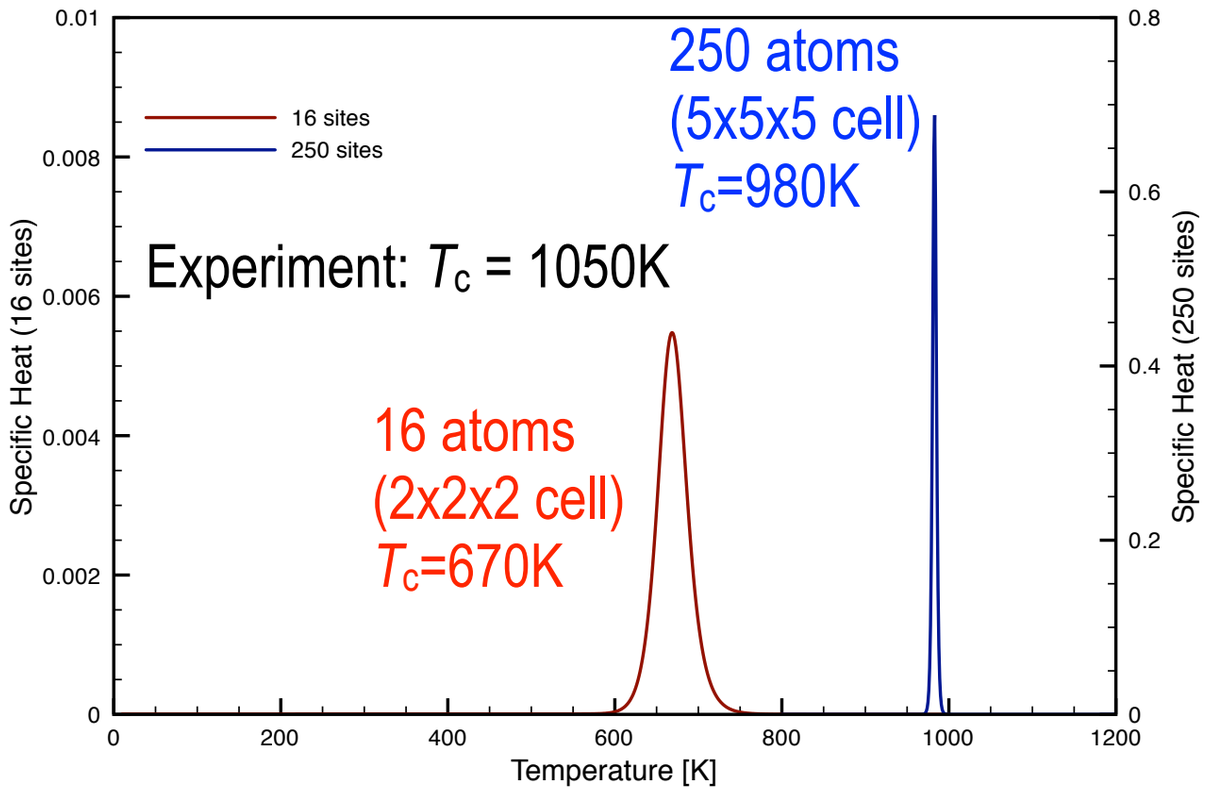
$$Z'(T) = g_0 \int g(E) e^{-E/(k_B T)} dE = g_0 Z$$

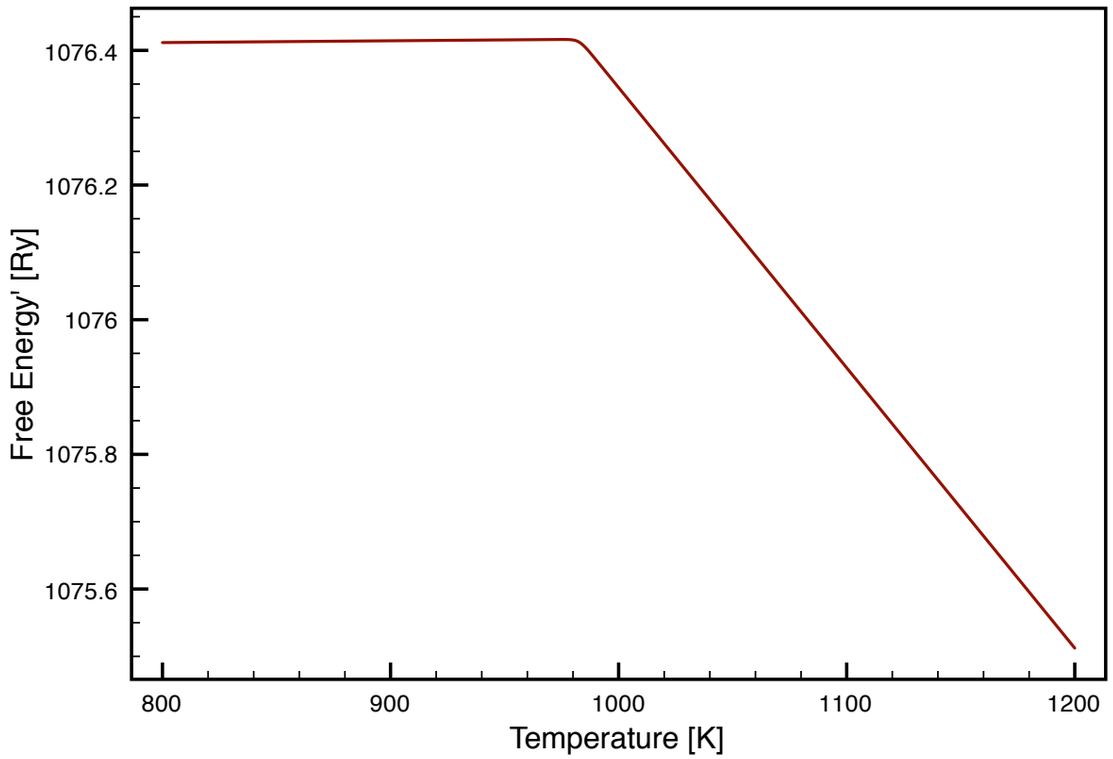
unknown normalization factor

$$F = -k_B T \ln Z \qquad S = -\frac{\partial F}{\partial T}$$

$$U = F + TS = F' + TS'$$

Specific heat $C = \frac{\partial U}{\partial T}$





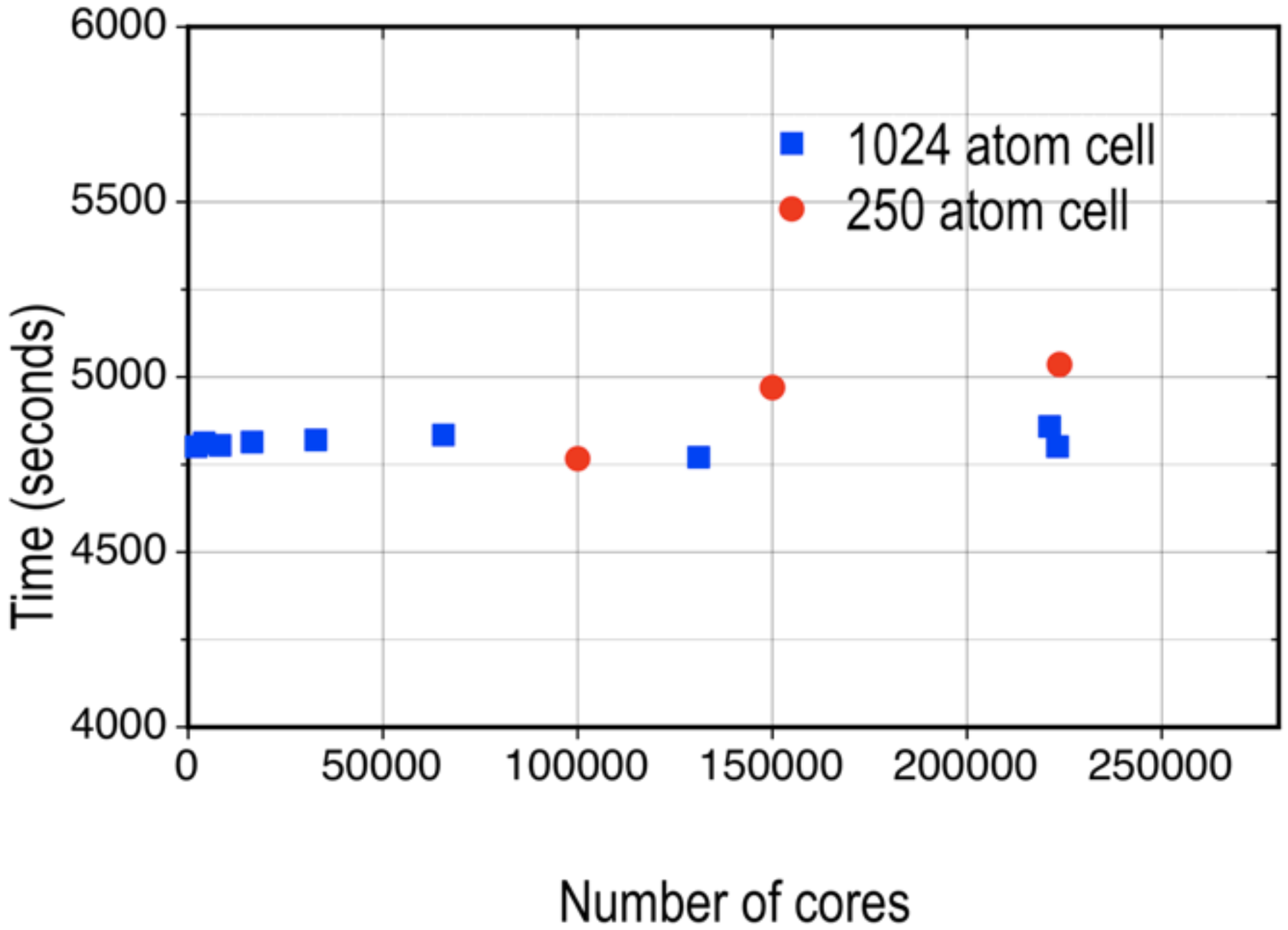
WL simulations for cubic Heisenberg model

$$E(\{\vec{S}_i\}) = \sum_{i \neq j} J \vec{S}_i \vec{S}_j$$

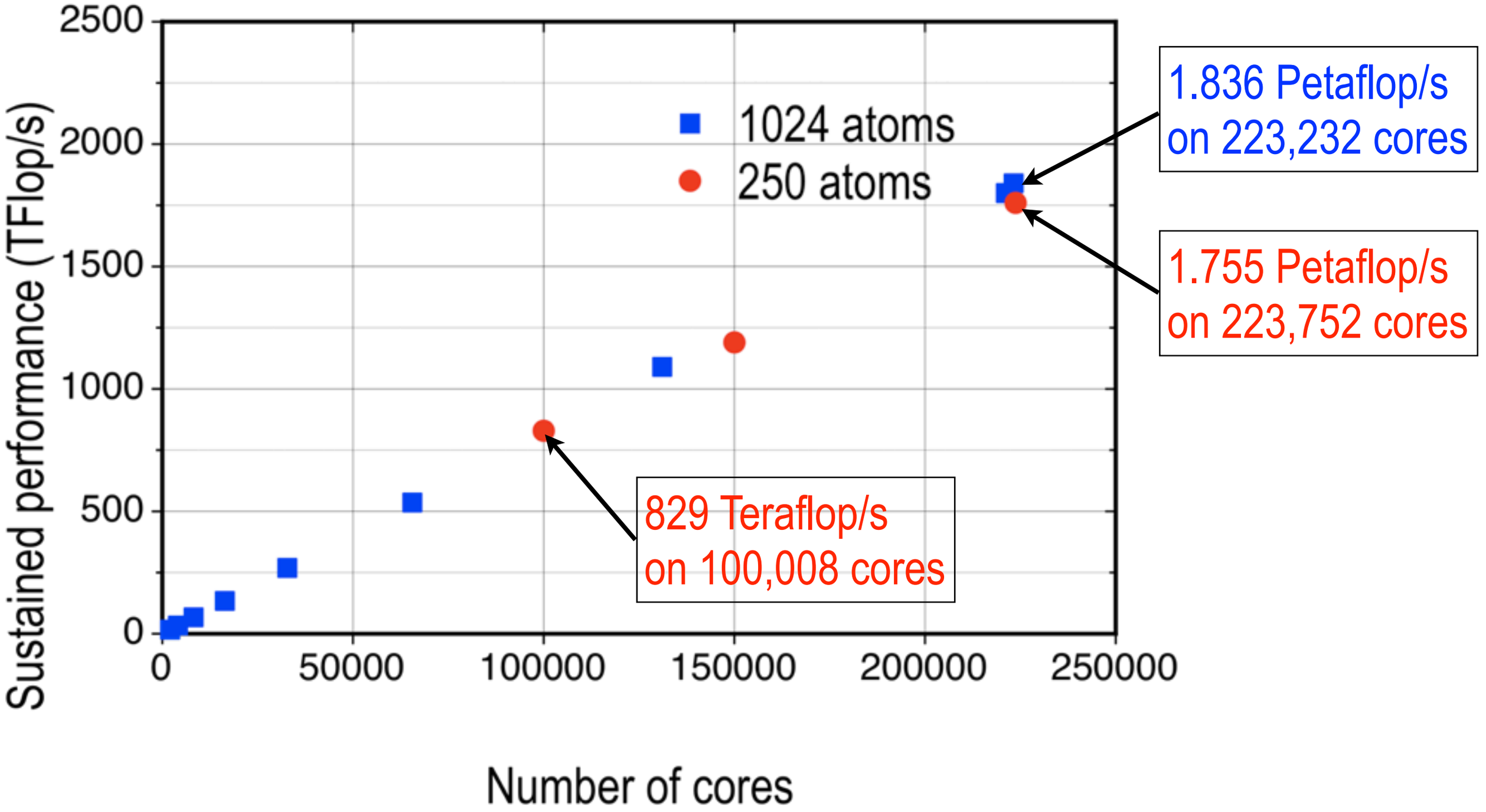
L	T_c (J)
2	**1.105**
3	1.340
4	1.370
5	**1.420**
6	1.465
7	1.460
8	1.490
∞	1.44

Upgraded Cray XT5 portion of Jaguar @ NCCS

Weak scaling on Cray XT5 (Jaguar)



Sustained performance of WL-LSMS on Cray XT5



Conclusions

- It is now possible to compute free energies in nanoscale systems
  - using ab initio methods based on Density Functional Theory
  - fully taking into account entropy
- First ab initio calculation of ferromagnetic transition temperature in Fe that does not rely on mean-field approximation
  - LDA answer based on WL-LSMS underestimate Tc by (only) 7%
- WL-LSMS code sustained 1.836 Petaflop/s (double precision) on 223,232 cores of the Cray XT5 system Jaguar